SELF-ASSOCIATION OF PHENOL IN NON-POLAR SOLVENTS

Kermit B. Whetsel and J. Harold Lady

Tennessee Eastman Co., Division of Eastman Kodak Co., Kingsport, Tenn. 37660

Although the self-association of phenol has been studied by a variety of methods, our knowledge of the thermodynamics of the process is still incomplete. Thermodynamic constants for the dimerization of phenol in carbon tetrachloride solution have been reported (1, 2), but comparable data for the formation of higher multimers are not available. Furthermore, the effects of solvents on the self-association process have not been reported.

The objective of the present work was to determine thermodynamic constants for the dimer and higher multimers of phenol in carbon tetrachloride and cyclohexane solutions. The intensity of the first overtone O-H stretching band of phenol was measured as a function of concentration and temperature in both solvents and the fit of the data to a variety of self-association models tested. A method was developed for calculating the approximate absorptivity of O-H end groups in linear associated species and for taking this factor into account in the determination of formation constants. The effects of concentration, temperature, and solvent upon the fundamental O-H stretching bands of phenol were investigated briefly.

EXPERIMENTAL

Equipment and Materials. Measurements in the fundamental and first overtone regions were made with Beckman IR-9 and Cary Model 14 spectrophotometers, respectively, equipped with thermostated cell holders. Spectral slit widths were approximately 2.3 cm^{-1} in the fundamental region and 6.4 cm^{-1} in the overtone region. Spectro grade cyclohexane was used as received. Reagent grade carbon tetrachloride was dried over molecular sieve Type 5A. Reagent grade phenol was distilled and stored in a desiccator over Drierite and phosphorous pentoxide. When not being used, all solutions were stored in glass-stoppered flasksin a desiccator.

Calculations. For the self-association equilibria $nC_1 \rightleftharpoons C_n$, the following equations apply:

$$K_n = \frac{C_n}{C^n} \qquad (1)$$

$$A/l = \epsilon_1 C_1 + \epsilon_2 K_2 C_1^2 + \text{---} + \epsilon_n K_n C_1^n = \epsilon_1 C_1 + \sum_{n=2}^{n=n} \epsilon_n K_n C_1^n \qquad (2)$$

$$C_A^s = C_1 + 2K_2 C_1^2 + 3K_3 C_1^3 + \text{---} + nK_n C_1^n = C_1 + \sum_{n=2}^{n=n} nK_n C_1^n \qquad (3)$$

where A is absorbance, l is path length, C_1 is monomer concentration, C_A^s is stoichiometric concentration, ϵ_1 is monomer absorptivity, and ϵ_n is the absorptivity of polymeric species. For the special case of $\epsilon_n = 0$, equations 2 and 3 reduce to

$$A/l = \epsilon_1 C_1 \tag{4}$$

and

$$C_A^\circ = A/l\epsilon_1 + \sum_{n=2}^{n=n} nK_n \, (A/l\epsilon_1)^n \tag{5}$$

The number of unknown parameters in Equation 5 can be reduced by imposing the restriction that the stepwise formation constants for all multimers above dimer are equal. This type of association is described by the expressions:

$$C_1 + C_{n-1} \rightleftharpoons^{K} C_n \qquad K = \frac{(C_n)}{(C_1)\ (C_{n-1})} \tag{6}$$

where $\underline{K}$ is independent of $\underline{n}$ when $\underline{n} > 2$. Under these conditions K_n is equal to K_2K^{n-2}, and the only unknowns in Equation 5 are K_2, K, and ϵ_1.

The values of ϵ_1 required for the solution of Equation 5 were determined by extrapolating plots of apparent absorptivity versus C_A° to infinite dilution. The formation constants were calculated using a computer and a standard least squares method for polynomials. The program used to solve the general form of Equation 5 allowed formation constants to be calculated for single multimers or any combination of multimers from dimer through octamer. The program used to solve the restricted form allowed the contribution of up to 20 species to be taken into account.

Equation 5 is not directly applicable when $\epsilon_n \neq 0$, but it can be used to determine formation constants by an iteration procedure as follows: Initial estimates of K_n are obtained by assuming than $\epsilon_n = 0$ and using Equation 5 in the normal manner. A small increment of end group absorptivity ($\Delta\ \epsilon_n = 0.05$ to 0.10) is assumed and a set of corrected A/l values generated by using the equation

$$(A/l)_{C(1)} = (A/l)_{obs} - \Delta\ \epsilon_n \sum_{n=2}^{n=n} K_n \, (l/\epsilon_1)^n \ \ (A/l)_{obs}^n \tag{7}$$

This set of values is substituted into Equation 5 to obtain second estimates of K_n. The second estimates of K_n and the first set of corrected A/l values are substituted into the right side of Equation 7 to obtain a second set of corrected A/l values. Successive estimates of K_n and corrections of A/l are made until the standard error of fitting Equation 5 passes through a minimum. The values of K_n giving the minimum error are taken as the best estimates of these quantities. The approximate end group absorptivity is equal to $\underline{N}(\Delta\ \epsilon_n)$, where $\underline{N}$ is the number of iterations required to obtain the minimum error. The best estimate of the end group absorptivity is calculated from the equation

$$(A/l)_{obs} = (A/l)_{C(N)} + \epsilon_n \sum_{n=2}^{n=n} K_n \, (l/\epsilon_1)^n \ (A/l)_{C(N)} \tag{8}$$

where $(A/l)_{C(N)}$ is the set of corrected A/l values which gives the minimum error in fitting Equation 5.

The iteration procedure was used only with the model involving dimerization and stepwise association constants, where $K_n = K_2K^{n-2}$. The results obtained when the method was tested with synthetic data are shown in Table I. While the method does not converge to the theoretical values, it yields values for the formation constants and ϵ_n that are within 5 and 20%, respectively, of the true values.

RESULTS

Spectral Data. Solutions of phenol above a few hundredths molar show three O-H bands in the fundamental region. The free O-H band is near 3612 cm^{-1} and the two bonded O-H bands are near 3500 and 3350 cm^{-1}. The band near 3500 cm^{-1} is normally assigned to a cyclic dimer species and the one near 3350 cm^{-1} to linear associated species. The relative intensity of the band near 3350 cm^{-1} increases with increasing concentration and decreasing temperature.

The principal feature of the first overtone spectrum is a free O-H band near 7050 cm^{-1} whose apparent absorptivity decreases as self-association occurs. Bonded O-H groups are evidenced only by a broad, weak band extending from about 7050 to 6000 cm^{-1}. The absorptivity of the monomer is approximately 50% greater in cyclohexane than in carbon tetrachloride. Self-association occurs more readily in the hydrocarbon solvent, however, and at concentrations above 0.1 or 0.2M the order of apparent absorptivities is reversed.

Model Fitting. In the initial attempts to find the best model, only the data for phenol concentrations less than 0.1M were used. Several different models gave satisfactory fits over this limited concentration range. But when the formation constants derived from these tests were applied to data for higher phenol concentrations, the agreement between calculated and observed absorbances deteriorated rapidly.

A variety of models were tested using data for phenol concentrations up to 0.65M in cyclohexane and 1.0M in carbon tetrachloride. The standard errors for the different models are shown in Table II. Several of the models which gave good fits over a limited range of concentration gave negative values for one or more constants when tested over the more extended range. The model involving a dimerization constant and equal stepwise association constants for higher multimers gave the best fit in both solvents.

In Figure 1 the fits of several different models are shown graphically. The good fit of the dimer-stepwise model and the poor fit of most of the other models are evident. These curves indicated that certain combinations of simpler models might give good fits, and subsequent calculations showed that a trimer-hexamer model did, indeed, provide a good fit. This model does not appear to be as plausible physically as the dimer-stepwise model, and it was not studied further.

Application of the end group correction to the data for the carbon tetrachloride system is illustrated by the curves in Figure 2. With the data taken at 2.5°, the minima in the standard error curves correspond to an end group absorptivity of approximately 0.3 l./mole-cm. The average value of ϵ_n determined at temperatures between 2.5 and 46° was 0.4 l./mole-cm., which is equivalent to $0.11\epsilon_1$.

When the end group correction was applied to the data for the cyclohexane system, the standard error of fit decreased at four temperatures but did not at three others. The maximum value for ϵ_n was $0.08\epsilon_1$ and the average was only $0.03\epsilon_1$. In view of these results, we do not feel that application of the correction to the data for the cyclohexane system is valid.

Thermodynamic Results. Plots of formation constants vs 1/T for dimerization and stepwise association are shown in Figure 3. The thermodynamic constants derived from the plots are summarized in Table III. The lines in Figure 3 for the carbon tetrachloride system represent data to which the end group correction was applied. In Table III the thermodynamic constants calculated for both the original and the corrected data are shown for comparison.

DISCUSSION

Coggeshall and Saier (3) found that a dimerization-stepwise association model adequately describes the effects of self-association on the fundamental O-H band of phenol in carbon tetrachloride solution. Our results obtained in the first overtone region confirm the validity of the model and show, in addition, that it is applicable to self-association in cyclohexane solution.

Our values of 0.94 and 3.25 l./mole for K_2 and K in carbon tetrachloride at 25° can be compared with values of 1.39 and 2.94 l./mole found by Coggeshall and Saier at ambient instrument temperature and with values of 0.70 and 0.83 l./mole reported by West and coworkers (1, 2) for K_2 at 25°. Our heat of dimerization of -5.03 kcal./mole is in excellent agreement with the value of -5.1 kcal./mole reported by Maguire and West (1). A more recent value of -3.6 reported by Powell and West (2) seems abnormally low. No direct comparison can be made for the heat of formation of higher multimers, but our value of -4.32 kcal./mole agrees well with an overall heat of association of -4.35 kcal./mole reported by Mecke (4). Mecke worked with relatively high concentrations of phenol, and his value is heavily weighted toward the stepwise heat of formation.

Both the dimerization constants and the stepwise formation constants are approximately twice as large in cyclohexane solution as in carbon tetrachloride solution. The heats of formation in the hydrocarbon solvent, however, are only 10 to 20% higher than those in the chlorinated solvent. Similar results have been obtained recently for a variety of hydrogen bonded complexes of phenol in these two solvents (5).

The average value of 0.4 l./mole-cm. found for the end group absorptivity in carbon tetrachloride solution is approximately 0.1 as large as the absorptivity of the free O-H group. This result indicates either that the O-H end groups interfere only slightly at the frequency where the monomer band occurs or that the concentration of end groups is much lower than one would expect on the basis of a linear association model. A low concentration of end groups could result from the formation of cyclic multimers or three dimensional aggregates. Most workers in this field have assumed that end group absorption is negligible but have recognized that the assumption might introduce major errors in the calculated formation constants. The present results show that the assumption is reasonably valid, at least in the first overtone region. Data recently presented by Bellamy and Pace (6) indicate that the end group absorptivity may be as large as $0.3\epsilon_1$ in the fundamental region.

The question of whether alcohols and phenols form linear or cyclic dimers, or both, has been discussed widely. Considerable evidence favoring the predominance of cyclic dimers has been presented, but recent work by Bellamy and Pace (6), Ibbitson and Moore (7), and Malecki (8) emphasizes the importance of linear dimers. Our thermodynamic results indicate that a significant fraction of the phenol dimer is in the linear form.

The apparent dimerization constant and heat of formation of the dimer are related to the individual values for the linear and cyclic forms as follows (9):

$$K_A = K_L + K_C \tag{10}$$

$$\Delta H_A = \frac{K_L(\Delta H_L) + K_C(\Delta H_C)}{K_A} \tag{11}$$

where the subscripts A, L, and C represent apparent, linear, and cyclic. If we assume that the heat of formation of the linear dimer is equal to the stepwise heat of formation of higher multimers, we can calculate values of ΔH_C, ΔS_C, and ΔS_L for various assumed ratios of K_L and K_C (Table IV). Making the reasonable assumption that ΔS_C is larger than ΔS_L but somewhat less than twice as large, we conclude that the ratio of K_L to K_C is at least 0.5 and possibly greater than unity.

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TABLE I

TEST OF METHOD FOR END GROUP CORRECTION (SYNTHETIC DATA)

	Theoretical	Calculated	
		Uncorrected	Corrected
ϵ_n	$1.53(0.3\epsilon_1)$	0	$1.22(0.24\epsilon_1)$
K_2	2.96	3.17	2.92
K	9.97	7.05	9.45
Standard Error	0	0.0069	0.0001

TABLE II

TEST OF MODELS FOR SELF-ASSOCIATION OF PHENOL

Model	Standard Error	
	Cyclohexane[a]	CCl_4[b]
Dimer	0.058	0.061
Trimer	.035	.032
Tetramer	.019	.010
Pentamer	.009	.013
Hexamer	.009	.029
Dimer-Trimer	----[c]	----[c]
Dimer-Tetramer	----[c]	----[c]
Dimer → Tetramer	----[c]	----[c]
Dimer → Pentamer	----[c]	----[c]
Dimer → Octamer	----[c]	----[c]
Dimer-Stepwise	.004	.005

[a] Phenol concentrations up to 0.65M at 22.2°.

[b] Phenol concentrations up to 1.0M at 20.7°.

[c] Negative values for one or more constants.

TABLE III

THERMODYNAMIC CONSTANTS FOR SELF-ASSOCIATION OF PHENOL

Thermodynamic Constant	Dimer Formation	Higher Multimer Formation
	Cyclohexane Solution	
$K_{25}°$, l./mole	2.10	6.68
ΔF, kcal./mole	- 0.44	- 1.13
ΔH, kcal./mole	- 5.63±0.21	- 5.22±0.13
ΔS, cal./mole-degree	-17.4	-13.7
	CCl_4 Solution (With End Group Correction)	
$K_{25}°$, l./mole	0.94	3.25
ΔF, kcal./mole	0.04	- 0.70
ΔH, kcal./mole	- 5.03±0.27	- 4.32±0.28
ΔS, cal./mole-degree	-17.0	-12.2
	CCl_4 Solution (Without End Group Correction)	
$K_{25}°$, l./mole	1.09	2.74
ΔF, kcal./mole	- 0.05	- 0.60
ΔH, kcal./mole	- 6.08±0.21	- 4.07±0.06
ΔS, cal./mole-degree	-20.2	-11.7

TABLE IV

THERMODYNAMIC CALCULATIONS FOR PHENOL DIMERIZATION

Assumed	CCl_4[a]			Cyclohexane[b]		
K_L/K_C	$-\Delta H_C$	$-\Delta S_C$	$-\Delta S_L$	$-\Delta S_C$	$-\Delta S_C$	$-\Delta S_L$
0	5.03	17.0	∞	5.63	17.4	∞
0.1	5.10	17.4	19.3	5.73	17.9	20.9
0.5	5.40	19.0	17.0	5.85	18.9	17.9
1.0	5.74	20.8	16.0	6.05	20.2	17.4
2.0	6.44	24.0	15.4	6.48	22.4	16.9

[a] ΔH_L = -4.32 kcal./mole

[b] ΔH_L = -5.22 kcal./mole

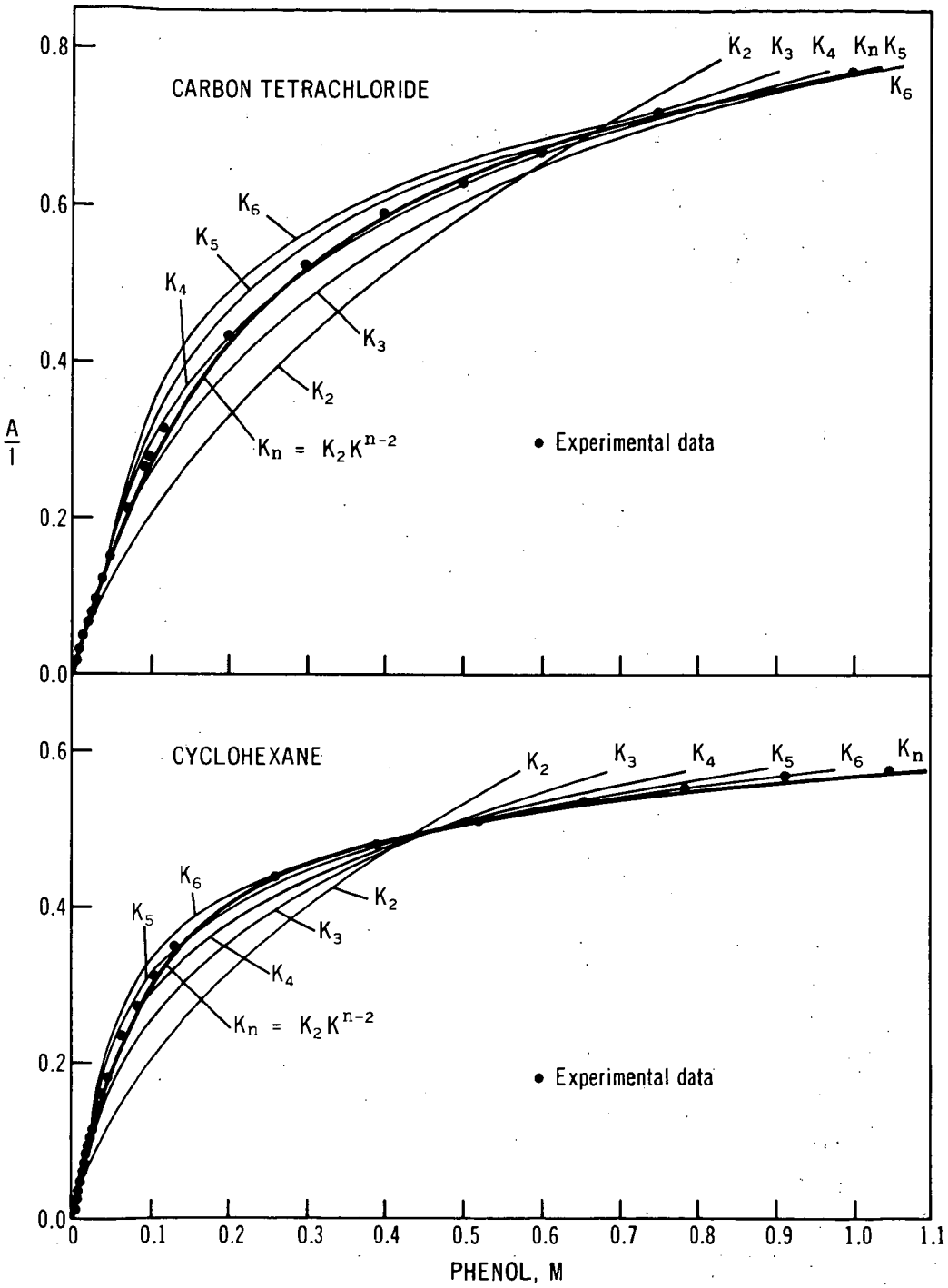

Figure 1. Fit of Experimental Data to Various Self-Association Models

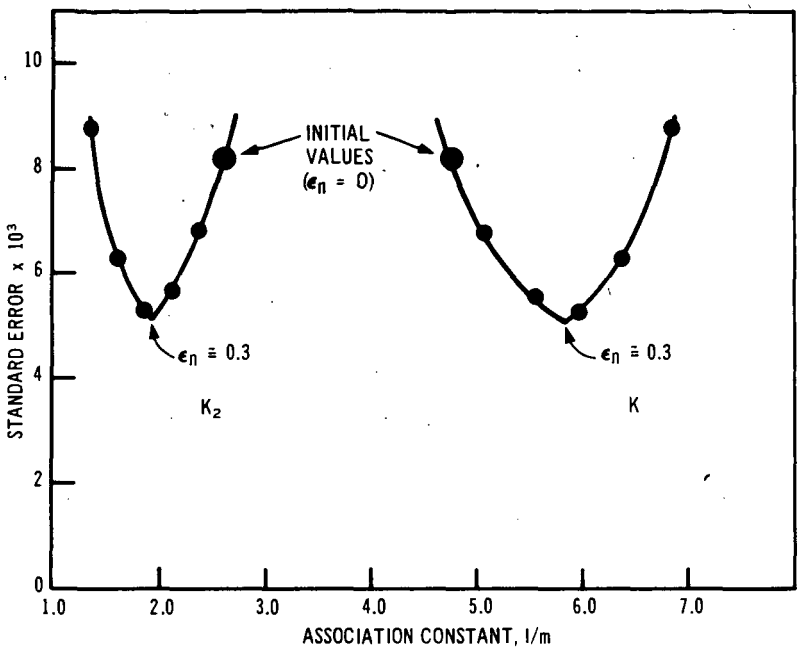

Figure 2. Correction for End Group Absorptivity (CCl_4 Solutions at 2.5°)

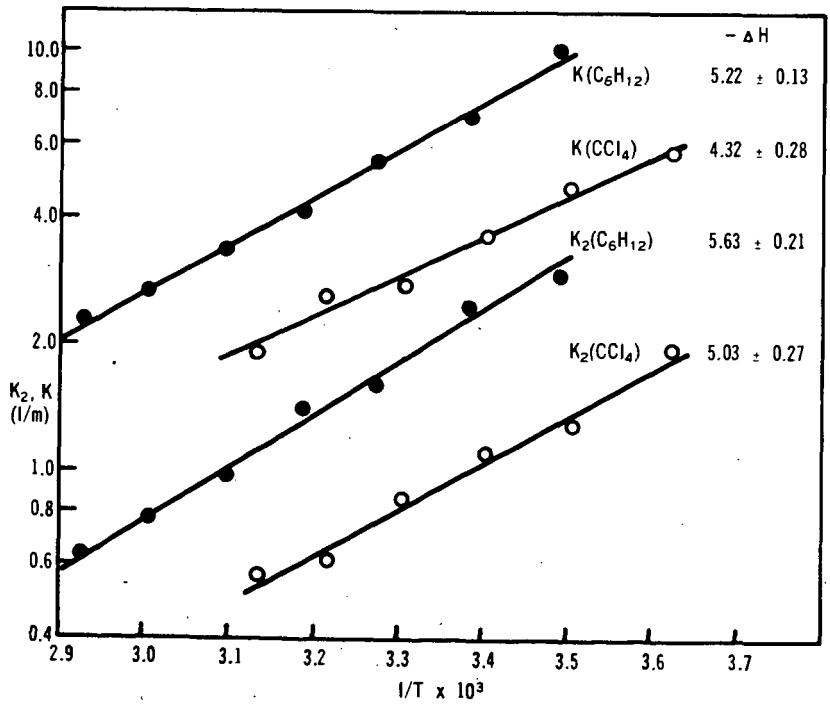

Figure 3. Enthalpies for Dimerization and Stepwise Association.